Sequence of phase formation in planar metal-Si reaction couples

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A correlation is found between the sequence of phase formation in thin-film metal-Si interactions and the bulk equilibrium phase diagram. After formation of the first silicide phase, which generally follows the rule proposed by Walser and Bené, the next phase formed at the interface between the first phase and the remaining element (Si or metal) is the nearest congruently melting compound richer in the unreacted element. If the compounds between the first phase and the remaining element are all noncongruently melting compounds (such as peritectic or peritectoid phases), the next phase formed is that with the smallest temperature difference between the liquidus curve and the peritectic (or peritectoid) point.

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The widespread use of thin films in modern electronic and optical devices has stimulated great interest in detailed understanding of thin-film interactions. The thin-film interactions induced by thermal annealing between Si and transition metals (TM) have, in particular, been thoroughly studied because of their application to Si integrated-circuit technology.[1,2] Typically in a planar TM-Si bilayer, the reaction produces a planar TM silicide which forms at temperatures well below the melting point of the silicide phase and grows to the total depletion of one of the starting elements. Walser and Bené[3] have proposed a rule based on the TM-Si phase diagram that predicts the first phase formed at the TM-Si interface. The rule has been found to hold for most of the TM-single-crystal Si interactions studied thus far. On the other hand, the last phase formed in a given system is always predictable from the phase diagram because equilibrium must ultimately prevail.[4] This letter addresses the question of what phases are formed after the first phase formation has fully consumed one element of a binary thin-film system, and in particular the metal-Si system.

The interaction between Si and transition metals can generally be described by the schematic diagram shown in Fig. 1. In the initial stage of reaction the first phase M_mSi_n forms at the Si-TM interface. After one of the elements (Si or metal) has been consumed in the growth of M_mSi_n, the reaction is driven toward the phases that are richer in the remaining element. If the thickness of Si is much greater than that of metal, a second phase richer in Si ($M_{x<m}Si_n$) will generally start to form at the Si-M_mSi_n interface. Most of the experiments of this type were carried out with metal films deposited on single-crystal Si substrates.[1] On the other hand, if the thickness of metal is much greater than that of Si, the next phase formed at the TM-M_mSi_n interface will be a more metal-rich silicide $M_{x>m}Si_n$. The experiments of this type are usually performed with metal films deposited on amorphous Si films on inert substrates.[4,5] The question of our concern is; what is the second phase formed at the interface between the silicide and the element (Si or metal) if more than one compound exists in the bulk phase diagram betweem the first silicide and the remaining element?

Phase formation requires nucleation as an initial step. Nucleation is believed to take place near the interfacial region where a concentration gradient varying from the silicide to the element is present. The existence of a concentration gradient in the interfacial region has been experimentally observed in the Ni-Si system.[6] The width of the interfacial region was estimated to be $\lesssim 20$ Å. The interfacial region is expected to have a concentration profile with compositions ranging from the silicide to the pure element. Nucleation of compounds within this composition range can occur, but usually only one of them will nucleate and grow to a measurable amount. As an example, consider the reaction between Pt and Si. The phase diagram of a Pt-Si system is shown in Fig. 2. The first phase observed is Pt_2Si, consistent

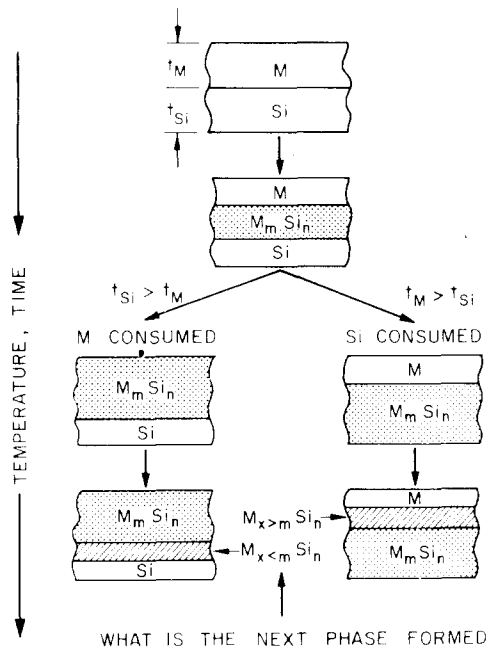

FIG. 1. Schematic diagram showing the phase formation in metal-Si interactions. The first phase, M_mSi_n, forms at the M-Si interface and then after one of the elements is consumed, the system is driven toward equilibrium by the formation of compounds richer in the remaining element.

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TABLE I. Sequence of observed phases formed in binary thin-film systems. The second phase formed is that with the smallest ΔT.

Source of binary bulk-phase diagram	Compuonds from bulk-phase diagram		Temperature difference ΔT(°C) (approximate)	Experimentally observed sequence of phase formation $T_{Si} > T_M, T_M > T_{Si}$		Ref.	First phase predicted by Walser-Bené rule
Hansen and Anderko	Ni_3Si	(NC)	50		3	(4)	
	Ni_5Si_2	(C)	0		2	(4)	
	Ni_2Si	(C)	0	1	1	(1)	Ni_2Si
	Ni_3Si_2	(NC)	300				
	NiSi	(C)	0	2		(1)	
	$NiSi_2$	(NC)	120	3		(1)	
Moffatt	Pd_5Si	(NC,C,?)	0-15		4	(14)	
	Pd_4Si(?)	(NC)	80		3	(14)	
	Pd_3Si	(C)			2	(5)	Pd_3Si (by Ref. 10)
	Pd_2Si	(C)		1	1	(1)	Pd_2Si (by Ref. 7)
	PdSi	(C)		2		(1)	
Hansen and Anderko and Shunk (see Fig.2)	Pt_3Si	(NC)	10		2	(4)	
	Pt_7Si_3	(NC)	50				
	Pt_2Si	(C)	0	1	1	(1)	Pt_2Si
	Pt_6Si_5	(NC)	200				
	PtSi	(C)	0	2		(1)	
Hansen and Anderko	Co_3Si	(NC)	30				
	Co_2Si	(C)		1		(1)	Co_2Si
	CoSi	(C)		2		(1)	
	$CoSi_2$	(C)		3		(1)	
Hansen and Anderko	Fe_3Si	(NC)	10		2	(11)	
	Fe_5Si_3	(NC)	220				
	FeSi	(C)		1	1	(1)	FeSi
	$FeSi_2$	(C)		2		(1)	
Moffatt	Cr_3Si	(C)			3	(11)	
	Cr_5Si_3	(C)			2	(11)	
	CrSi	(NC)	50				
	$CrSi_2$	(C)		1	1	(1)	$CrSi_2$
Moffatt	V_3Si	(C)			3	(11)	
	V_5Si_3	(C)			2	(11)	
	V_5Si_4	(NC)	300				
	VSi_2	(C)		1	1	(1)	VSi_2
Elliott	Hf_2Si	(NC)	200		3	(11)	
	Hf_5Si_3	(NC)	20		2	(11)	
	Hf_3Si_2	(NC)	40				
	HfSi	(C)		1	1	(1)	HfSi
	$HfSi_2$	(NC)	100	2		(1)	
Moffatt	Pd_5Ge	(NC)	150		3	(14)	
	Pd_3Ge	(NC)	300				
	$Pd_{25}Ge_9$	(NC)	40		2	(14)	
	Pd_5Ge_2	(NC)	150				
	Pd_2Ge	(C)		1	1	(13)	
	PdGe	(C)		2		(13)	PdGe
Hansen and Anderko	Au_4Al	(NC)	10		2	(12)	
	Au_5Al_2	(NC)	20	1	1	(12)	
	Au_2Al	(C)		2		(12)	Au_2Al
	AuAl	(NC)	200				
	$AuAl_2$	(C)		3		(12)	

with the prediction of the Walser and Bené rule. On the Si-rich side, two compounds with compositions Pt_6Si_5 and PtSi exist. The experimental results show that it is the congruently melting phase PtSi that forms at the Pt_2Si-Si interface rather than the compositionally neighboring phase Pt_6Si_5. On the Pt-rich side, three compounds Pt_7Si_3, Pt_3Si, and Pt_4Si (the existence of this phase is in doubt, as indicated by the question mark in the phase diagram in Fig. 2) are present. The second phase formed at the Pt_2Si-Pt interface is Pt_3Si rather than the compositionally neighboring phase Pt_7Si_3.[4] Both Pt_7Si_3 and Pt_3Si are peritectic compounds. The temperature difference ($\equiv\Delta T$) between the liquidus curve and the peritectic for these phases are ~ 50 °C ($\simeq$1036–986 °C) for Pt_7Si_3 and ~ 10 °C ($\simeq$880–870 °C) for Pt_3Si. The experi-

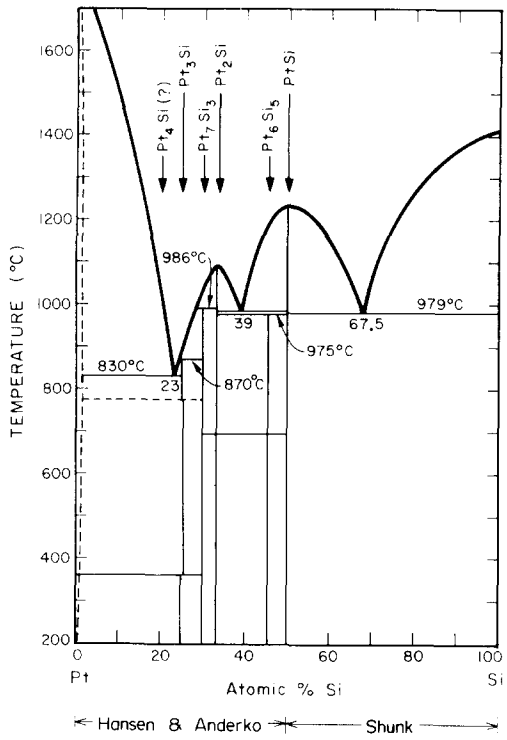

FIG. 2. Equilibrium-phase diagram of the Pt-Si system. [From Shunk (Ref. 9) for Pt$\geqslant$50 at. % and Hansen and Anderko (Ref. 7) for Pt $\leqslant$50 at %.]

mental results in the Pt-Si system thus indicate that nucleation and growth for the second phase favors the congruently melting compound PtSi (for which $\Delta T = 0$) and the low ΔT peritectic compound Pt_3Si.

Based on this concept, a systematic survey on the sequence of phase formation in Si-TM interactions reported in the literature has been carried out. Table I summarizes the results for eight TM-Si systems together with those for Pd-Ge and Au-Al. The first column gives the reference to the bulk phase diagram[7–10] used. The second column lists the binary compounds given in the phase diagrams in the sequence of decreasing metal content. The letter C in the parenthesis indicates a congruently melting compound and NC a noncongruently melting compound. The third column gives the temperature difference ΔT between the liquidus curve and the peritectic (or in some cases peritectoid) point for the noncongruently melting compounds; for the congruently melting compound ΔT is set equal to zero by logical extension of the definition. The fourth column lists the sequence of experimentally observed phase for the two conditions where the amount of either one or the other of the two elements is largest, and the literature reference used. The first phase predicted by the Walser-Bené rule is shown in the last column of the Table.

The first general observation from the Table is that the first phase formed is always the same irrespective of the thickness ratio between the Si and metal layers. It is that fact that permits the formulation of rule to predict the first phase formed based on the knowledge of only the two constituting elements and not their amount, as is done in the rule of Walser-Bené.[3] The second phase formed at the interface between the first phase and the remaining element is always the nearest congruently melting compound richer in the unreacted element (for example, PtSi for the Pt_2Si/Si case). If these compounds are all noncongruently melting phases, the next phase formed is the one with the lowest ΔT (for example, Pt_3Si for the Pt_2Si/Pt case). This correlation is found to be true for the sequential phase formation for all the cases reported in Table I. The evidence contained in the Table thus suggests the formulation of the following rule: *The second phase formed is the compound with the smallest ΔT that exists in the phase diagram between the composition of the first phase and the unreacted element.*

We note that the larger the ΔT value for a peritectic phase is, the larger the *compositional* difference ($\equiv \Delta c$) tends to be between the solid peritectic compound and the liquidus phase at the peritectic temperature. For example, for Pt_7Si_3, $\Delta T \simeq 50$ °C, and the difference Δc in composition between Pt_7Si_3 and the resulting liquid along the 986 °C tie-line is $\approx$2-at. %Si. For Pt_3Si, the difference in composition between Pt_3Si and the resulting liquid at 870 °C is nearly zero (see Fig. 2). We speculate that a small difference in composition between the peritectic and the liquidus phase at the peritectic temperature yields a low-energy barrier for nucleation because only small compositional fluctuations are required for nucleation. For congruently melting phase, the composition fluctuation for nucleation is essentially nil; therefore it is the easiest phase to form at the interface. The phase-formation rule described above is consistent with the concept of graded silicide-element interface, where phase nucleation is a competitive process due to variation of concentration in the interfacial region.

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[1]K. N. Tu and J. W. Mayer, in *Thin Film - Interdiffusion and Reactions*, edited by J. M. Poate, K. N. Tu, and J. W. Mayer (Wiley, New York, 1978), Chap. 10.
[2]G. Ottaviani, J. Vac. Sci. Technol. **16**, 1112 (1979).
[3]R. M. Walser and R. W. Bené, Appl. Phys. Lett. **28**, 624 (1976).
[4]C. Canali, G. Majni, G. Ottaviani, and G. Celotti, J. Appl. Phys. **50**, 255 (1979).
[5]C. Canali, L. Silvestri, and G. Celotti, J. Appl. Phys. **50**, 5768 (1979).
[6]P. J. Grunthaner, F. J. Grunthaner, and J. W. Mayer, in *Proceedings of the 7th Annual PCSI Conference*, edited by R. S. Bauer (Estes Park, Colorado, January 1980); in J. Vac.Sci. Technol. **17**, 924 (1980).
[7]M. Hansen and K. Anderko, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1965).
[8]R. P. Elliott, *Constitution of Binary Alloys, First Supplement* (McGraw-Hill, New York, 1965).
[9]F. A. Shunk, *Constitution of Binary Alloys, Second Supplement* (McGraw-Hill, New York, 1969).
[10]W. G. Moffatt, *Handbook of Binary Phase Diagrams* (General Electric Company, New York, 1978).
[11]Results on Pt, Ni, and Pd are from Canali *et al.* (Refs. 4 and 5). Results on Fe, Cr, V, and Hf were obtained at Caltech. Results on Au-Al and Pd-Ge are from private communications with G. Ottaviani.
[12]S. U. Campisano, G. Foti, E. Rimini, S. S. Lau, and J. W. Mayer, Philos. Mag. **31**, 903 (1975).
[13]M. Wittmer, M.-A. Nicolet, and J. W. Mayer, Thin Solid Films **42**, 51 (1977).
[14]F. Nava, G. Majni, G. Ottaviani, and E. Galli, (unpublished).